

(54) PRODUCTION OF THERMOSETTING PHENOLIC RESIN

(11) 5-279441 (A) (43) 26.10.1993 (19) JP
 (21) Appl. No. 4-108630 (22) 31.3.1992
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 (51) Int. Cl.⁵ C08G8 28

PURPOSE: To produce a thermosetting phenolic resin having high thermal curing rate and exhibiting high fluidity in molten state.

CONSTITUTION: A powdery phenolic resin is made to react with formaldehyde in water in the presence of calcium hydroxide or barium hydroxide at 40-55°C. The powdery phenolic resin is a powdery resin consisting of a condensation product of phenol and formaldehyde, composed of spherical primary particles having particle diameter of 0.1-150 μ m and their secondary agglomerate and having a methanol solubility of $\geq 70\%$ defined by the weight ratio of dissolved resin when 10g of the resin is heated and refluxed in 500mL of essentially anhydrous methanol.

(54) URETHANE RESIN COMPOSITION

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 (21) Appl. No. 4-80721 (22) 2.4.1992
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 (51) Int. Cl.⁵ C08G18/32; F16F15/02

PURPOSE: To provide the subject composition composed of a specific mixed polyol and a polyisocyanate compound and giving a vibration-damping material having excellent vibration-damping performance over a wide temperature range from normal temperature to high temperature and free from generation of ill odor and volatile component even at high temperature.

CONSTITUTION: The objective composition is composed of two liquid components consisting of (A) a liquid containing a mixed polyol having a hydroxyl value of 200-300mgKOH/g and produced by mixing 30-70wt.% of castor oil with 70-30wt.% of a polyfunctional ricinolate-type polyol and (B) a liquid containing a polyisocyanate compound. The equivalent ratio of the hydroxyl group of the component A to the NCO group of the component B is 0.6-1.2. The polyfunctional ricinolate-type polyol can be produced by modifying castor oil with a polyhydric alcohol such as glycerol. The component B is preferably an aromatic polyisocyanate compound such as diphenylmethane diisocyanate. The above composition is molded usually at a temperature between room temperature and 100°C.

(54) PRODUCTION OF POLYCAPROLACTONE CONTAINING URETHANE BOND

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 (51) Int. Cl.⁵ C08G18 42, C08G63 08, C08G63 685, C08G63 91

PURPOSE: To obtain the subject bio-decomposable polycaprolactone having high toughness and physical properties suitable as films, molded materials, etc., by reacting a specific polycaprolactone with a specific amount of a polyvalent isocyanate in molten state at or above the melting point of the polycaprolactone.

CONSTITUTION: The objective polycaprolactone is produced by reacting (A) 100 pts.wt. of a polycaprolactone having a number-average molecular weight of $\geq 5,000$ (preferably $\geq 10,000$) with (B) 0.1-5 pts.wt. of a polyvalent isocyanate (preferably aliphatic or cycloaliphatic diisocyanate) in an inert gas in molten state at a temperature (150-250°C) above the melting point of the component A.

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(54)【発明の名称】 ウレタン結合を含むポリカプロラク톤の製造方法

(57)【要約】

【構成】 数平均分子量が5,000以上のポリカプロラク톤に、その融点以上の熔融状態で、該ポリカプロラク톤100重量部当り0.1~5重量部の多価イソシアナートを反応させる。

【効果】 本発明の方法によれば、フィルム、成形品、繊維などを成形することができる、少量のウレタン結合を含むポリカプロラク톤をゲル化を生じることなく製造することができ、このポリカプロラク톤から成形されたフィルムはすぐれた引張り強さを有し、かつ生分解性である。

【特許請求の範囲】

【請求項1】 数平均分子量が5,000以上のポリカプロラクトンに、その融点以上の熔融状態で、該ポリカプロラクトン100重量部当り0.1～5重量部の多価イソシアナートを反応させることを特徴とするウレタン結合を含むポリカプロラクトンの製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、強靱なフィルム、成形品、繊維などの各種用途に十分な物性を有し、しかも生分解可能なウレタン結合を含むポリカプロラクトンの製造方法に関するものである。

【0002】

【従来の技術】生分解が可能であるプラスチックとして、ポリカプロラクトンがあることはよく知られている。このポリカプロラクトンは、主としてワイヤーを混入して剛性を付与し、使い捨て容器などに用いられている。しかし、ポリカプロラクトンは、生分解性プラスチックの用途として最も要望されている包装フィルム分野には、未だ進出していない。理由の一つはコスト高にもあるが、主な理由は、これまでフィルムとして十分な物性を示すポリマーが得られないからに他ならない。

【0003】

【発明が解決しようとする課題】本発明は、機械的強度に優れたフィルム、成形品、繊維などを成形することのできるウレタン結合を含むポリカプロラクトンの製造方法を提供することを目的とする。

【0004】

【課題を解決するための手段】本発明者は、ポリカプロラクトンの強度を高めて各種用途に有用な、特にフィルム分野でも有用なポリカプロラクトンを得るために研究を行った結果、数平均分子量が5,000以上で、末端基が実質的にヒドロキシル基であるポリカプロラクトンに、ポリカプロラクトンの融点以上の熔融状態で、少量の多価イソシアナートを添加、反応させることにより、上記目的が有効に達成され、フィルムとしても十分に物性を示す少量のウレタン結合を含むポリカプロラクトンが得られることを見出し、本発明を完成することができた。

【0005】即ち、本発明は、数平均分子量が5,000以上のポリカプロラクトンに、その融点以上の熔融状態で、該ポリカプロラクトン100重量部当り0.1～5重量部の多価イソシアナートを反応させることを特徴とするウレタン結合を含むポリカプロラクトンの製造方法に関する。

【0006】数平均分子量が5,000以下のポリカプロラクトンは、ポリウレタ、用がけ材等として公知であり、塗料、繊維、プラスチックの各用途に供されていることはよく知られている。しかし、これら既知の、いわゆるポリマー的な数平均分子量のポリカプロラクトン

は、必然的に末端ヒドロキシル基が多く、十分な物性を得るためには多価イソシアナートを5重量部（ポリカプロラクトン100重量部に対して）以上用いなければならぬ。そのような割合での熔融添加では必ずゲル化を起し、目的とするポリカプロラクトンを得ることはできない。ゲル化しない程度の多価イソシアナートの添加量では、目的とする物性を有するポリカプロラクトンを得ることができない。

【0007】本発明者らも、数平均分子量が5,000以上、望ましくは10,000以上のポリカプロラクトンを用いる理由は、そのような高分子量領域では、必然的に単位体積当りの末端ヒドロキシル基は減少し、そのようなポリカプロラクトンに、末端ヒドロキシル基と反応するに足る多価イソシアナートを、熔融添加することによっても、ゲル化せずに目的とするポリマーを得ることかできた事実によるものである。従って、ポリカプロラクトンの数平均分子量が増大すれば、それに従って多価イソシアナートの添加量は減少する。

【0008】本発明で用いるポリカプロラクトンは、数平均分子量が5,000以上、望ましくは10,000以上のものであり、市販品としては例えばタイセル化学工業(株)社製のプラクセルH-1(商品名)、プラクセルH-4(商品名)などを使用することかできる。

【0009】本発明に利用可能な多価イソシアナートは、一般に市販されているジイソシアナート、並びにジイソシアナートと多価アルコールとの付加体（例えばヘキサメチレンジイソシアナートとトリメチロールプロパンの付加体）、或はイソシアナートの3量体（例えばヘキサメチレンジイソシアナートの3量体）である。これらの多価イソシアナートのうち、特にジイソシアナートが好適であり、それらの例としては、例えば2,4-トリレンジイソシアナート、2,4-トリレンジイソシアナートと2,6-トリレンジイソシアナートとの混合ナートと2,6-トリレンジイソシアナート、1,5-ナフチレンジイソシアナート、キシリレンジイソシアナート、ヘキサメチレンジイソシアナート、イソホロキシイソシアナート、ホスホキシイソシアナート、イソシアナート、ホスホキシイソシアナート、ホスホキシイソシアナートなどかあげられる。特に脂肪族、或は環状脂肪族のジイソシアナートが着色が少なく好ましい。

【0010】多価イソシアナートの使用割合は、ポリカプロラクトン100重量部に対して0.1～5重量部、望ましくは0.5～3重量部である。多価イソシアナートの使用割合が0.1重量部未満では、本発明の効果が得られず、また5重量部より多い場合はゲル化の危険が生じる。

【0011】ポリカプロラクトンと多価イソシアナートの反応は、150℃以上250℃以下のポリカプロラクトンの熔融状態で、不活性ガス中に行うことが望ましい。

【0012】本発明により得られる少量のウレタン結合

を含むポリカプロラクトン)は、フィルム、成形品、繊維など、所望の形態に成形することができ、しかも生分解性である。

【0013】また、本発明の少量のウレタン結合を含むポリカプロラクトンの実用化の際には、必要に応じて、フィラー、補強材、着色剤、滑剤、ポリマーなどを併用できることは勿論である。

【0014】

【実施例】次に本発明の理解を助けるために、以下に実施例を示す。

【0015】なお、分子量測定は、GPCに依った。条件は次の通り。

使用機種

Shodex GPC SYSTEM-11 (昭和電工社製)

溶離液

5mM CF_3COONa , HFIP (ヘキサフロロイソプロパノール)

カラム

サンゲルカラム

HFIP-800P

HFIP-80M \times 2本

リファレンスカラム

HFIP-800R \times 2本

カラム温度

40℃

流量

1.0ml/min

検出器

Shodex RI

スタンダード

PMMA (Shodex STANDARD M-75)

【0016】実施例1

攪拌機、還流コンデンサー、分液ロート、温度計付ガス導入管を付した1lのセパラブルフラスコに、ポリカプロラクトンとして、ダイセル化学工業(株)社製の商品 *

*名フラクセルH-1 (カタログ値の数平均分子量1万、実測値9,400)を300g仕込み、温度200℃、窒素気流中でヘキサメチレンジイソシアナート5gを加えた。粘度は急速に増加したが、ゲル化はしなかった。

【0017】得られた少量のウレタン結合を含むポリカプロラクトン(A)の数平均分子量は27,000、重量平均分子量は104,000であった。ポリカプロラクトンの融点は60℃であったが、ウレタン結合を含むポリカプロラクトンの融点は明確ではなかった。

10 【0018】3倍に一軸延伸して得られた厚さ約60μmのポリカプロラクトン(A)のフィルムの引張り強さは、16.1~17.4kg/mm²、伸び率は200%以上であった。

【0019】一方、未処理のフラクセルH-1からのフィルムは、延伸途中で破断し、所望のフィルムが得られなかった。

【0020】実施例2

ポリカプロラクトンとして、ダイセル化学工業(株)社製の商品名フラクセルH-4 (カタログ値の数平均分子量4万~6万、実測値30,000)を300g、実施例1と同様の装置に仕込み、温度200℃、窒素気流中でジフェニルメタンジイソシアナート3gを加えた。粘度は急速に増大したがゲル化はしなかった。

【0021】得られた少量のウレタン結合を含むポリカプロラクトン(B)の数平均分子量は51,000、重量平均分子量は155,000、黄褐色ワックス状であった。

【0022】3倍に一軸延伸した厚さ50μmのフィルムの引張り強さは16.1~18.0kg/mm²、伸び率は150~170%で頗る強靱であった。

30

【0023】

【発明の効果】本発明の方法によれば、フィルム、成形品、繊維などを成形することができる、少量のウレタン結合を含むポリカプロラクトンをゲル化を生じることなく製造することができ、このポリカプロラクトンから成形されたフィルムは優れた引張り強さを有し、かつ生分解性である。

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CLAIMS

[Claim(s)]

[Claim 1] The microorganism collapsibility thermoplastics film weld field which makes a matrix resin 50 % of the weight - 90 % of the weight of microbially degradable thermoplastics, and is characterized by piling up mutually the film which comes to carry out the mixed variance of 50 % of the weight - the 10 % of the weight of the denaturation polyolefine system resins, carrying out heat weld of the part, and coming to form the weld section and the non-welding section into the matrix resin.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] this invention relates to the microorganism collapsibility thermoplastics film weld field.

[0002]

[Description of the Prior Art] The microorganism collapsibility thermoplastics film which mixed the poly-caprolactone which is microorganism collapsibility thermoplastics, and polyethylene is already proposed (Japanese Patent Application No. 281317 [two to]). The problem that the heat-sealing intensity (weld intensity) of a film falls remarkably produces this film as the loadings of polyethylene increase, although excelled in the microorganism collapsibility to be sure. On the other hand, while **** physical properties, such as **** breaking strength, **** elongation percentage, etc. of a film, fall remarkably as the loadings of polyethylene fall, the problem of a part of front face exfoliating by slight friction, or milking, when a film is pulled is produced. Therefore, the film weld fields, such as a bag-like object which carries out heat weld of such a microorganism collapsibility thermoplastics film, and is obtained, and a glove, an air enclosure pad, were not what should still be carried out satisfactory in respect of practicality.

[0003]

[Problem(s) to be Solved by the Invention] Let it be the technical problem to offer the microorganism collapsibility thermoplastics film weld field excellent in the practicality which is not milked when it pulls further, as it excels in a heat-sealing intensity and **** physical properties and a part of front face exfoliated by slight friction etc., while this invention solved simultaneously the problem of the lowness of a heat-sealing intensity, and the badness of **** physical properties looked at by the microorganism collapsibility thermoplastics film weld field and excelling in the microorganism collapsibility without, and.

[0004]

[Means for Solving the Problem] This invention persons came to complete this invention, as a result of repeating a research zealously that the aforementioned technical problem should be solved. That is, according to this invention, the microorganism collapsibility thermoplastics film weld field which makes a matrix resin 50 % of the weight - 90 % of the weight of microbially degradable thermoplastics, and is characterized by piling up mutually the film which comes to carry out the mixed variance of 50 % of the weight - the 10 % of the weight of the denaturation polyolefine system resins, carrying out heat weld of the part, and coming to form the weld section and the non-welding section into the matrix resin is offered.

[0005] What a well-known thing is shown [what] conventionally, for example, carried out copolymerization of the polyamide of low molecular weight to aliphatic polyester resin and aliphatic polyester in block as a microbially degradable thermoplastic resin (only henceforth a microbially degradable resin) which is the film material of this invention, polyvinyl alcohol, etc. are mentioned. The polycondensation object of the multiple-valued carboxylic acid containing the divalent carboxylic acid

of an aliphatic system and the polyhydric alcohol containing an aliphatic system diol, the polycondensation object of a hydroxy aliphatic carboxylic acid, and the ring-opening-polymerization object of lactone are included by aliphatic polyester resin, and the homopolymer and copolymer which are guided from an ethylene ***** peat, propiolactone, a caprolactone, beta-hydroxybutyric acid, etc. are illustrated as the example, for example. Two or more sorts can be mixed and used for these polymers. Moreover, each of these polymers is understood by operation of lipase etc. an added water part.

[0006] As a denaturation polyolefine system resin in this invention, a carbonyl group inclusion ethylene system unsaturation monomer is introduced into the principal chain or side chain of polyolefin resin with meanses, such as graft copolymerization, a block copolymerization, random copolymerization, or terminal processing. What is independent or contains a carboxylic acid, a carboxylate, a carboxylic-acid anhydride, a carboxylate, a carboxylic-acid amide, a carboxylic-acid imide, an aldehyde, a ketone, etc. as a carbonyl group inclusion ethylene system unsaturation monomer in combination, such as a cyano group, a hydroxy group, an ether machine, and an oxy-run ring, for example is illustrated. It is as follows when these examples are shown.

[0007] An acrylic acid, a methacrylic acid, a maleic acid, a fumaric acid, a crotonic acid, an itaconic acid, Ethylene system unsaturated-carboxylic-acid; maleic anhydrides, such as a citraconic acid, 5-norbornene -2, and 3-dicarboxylic acid, Anhydrous citraconic-acid and 5-norbornene -2, 3-dicarboxylic-acid anhydride, Ethylene system unsaturation anhydrous carboxylic-acid; acrylamides, such as tetrahydro phthalic anhydride, Ethylene system unsaturation amides, such as methacrylamide and maleimide, or imide; ***** , Ethylene system unsaturation aldehydes, such as a methacrolein, a vinyl methyl ketone, and a vinyl butyl ketone, or a ketone; ethyl acrylate, A methyl methacrylate, acrylic-acid 2-ethylhexyl, maleic-acid monochrome, or a G ethyl, Vinyl acetate, a propionic-acid vinyl, a gamma-hydroxy methacrylic-acid propyl, Ethylene system unsaturation ester, such as a beta-hydroxy ethyl acrylate, glycidyl acrylate, glycidyl methacrylate, beta-N-ethylamino ethyl acrylate, and diethylene-glycol dimethacrylate etc. The denaturation polyolefine system resin preferably used in this invention is the copolymer of the vinyl monomer and the olefins, such as ethylene and a propylene, which have ester combination of vinyl acetate, acrylate, methacrylate, etc.

[0008] The content of the carbonyl group inclusion ethylene system unsaturation monomer in the denaturation polyolefine system resin used by this invention is 0.5 - 40 % of the weight preferably 0.01 to 45% of the weight. Moreover, as for this carbonyl group inclusion ethylene system unsaturation monomer, it is preferably good to specify in 0.5 - 20% of the weight of a domain 0.01 to 25% of the weight among [all] a resin. In addition, the polyolefine system resin which is not denaturalizing can be included in the above-mentioned denaturation polyolefine system resin. In this case, as for mixed proportion, it is good to specify the content of the above-mentioned monomer in mixture to 0.5 - 20% of the weight like the above. As a non-denatured polyolefine system resin, a branching low density polyethylene, a straight chain low density polyethylene, a high density polyethylene, polypropylene, a polybutene, a propylene-ethylene copolymer, a propylene-butene copolymer, etc. are mentioned, for example.

[0009] A microbially degradable resin turns into a matrix resin, and the resin film which constitutes the film weld field of this invention carries out the mixed variance of (1) denaturation polyolefine system resin or (2) denaturation polyolefine system resin, and the polyolefine system resin (these resin (1) and (2) are only also hereafter called polyolefine system resin) into it. That is, it has the structure where the polyolefine system resin was covered with the microbially degradable resin. therefore, since the new front face exposed after the surface section consists of a microbially degradable resin and the surface section carries out microbial degradation is a microbially degradable resin similarly, such a resin film does not have microbial degradability -- it is -- it is -- in spite of including the inferior polyolefine system resin, the collectively excellent microorganism collapsibility is shown

[0010] The film which makes the aforementioned **** microbial degradability resin a matrix can be obtained by fabricating the melting kneading object of a microbially degradable resin and a polyolefine system resin in a film configuration. In this invention, when carrying out the film molding of the

aforementioned melting kneading object, as for the molding, it is desirable to adopt an extrusion. As this extrusion method, a tubular film process and a T die method are illustrated. When obtaining the above-mentioned resin film, as for a melting kneading object, it is desirable to extrude from the die at the nose of cam of an extruder to a low-pressure-zone region on the conditions with which it is satisfied of the following formula (1) and a formula (2). The film from which the microbially degradable resin became the matrix by this can be obtained easily.

$$10 > \eta(B) / \eta(A) \geq 1 \quad (1)$$

$$(\text{Preferably } 5 > \eta(B) / \eta(A) \geq 1)$$

$$\eta(A) \geq 500 \quad (2)$$

$\eta(A)$ shows the viscosity (poise) of the microbially degradable resin in an extrusion temperature among the aforementioned formula, and $\eta(B)$ shows the viscosity (poise) of the polyolefine system resin in an extrusion temperature. It can obtain by choosing the concrete modality containing the molecular weight of a microbially degradable resin or a polyolefine system resin, and also the extrusion conditions expressed with the aforementioned formula (1) and (2) can be acquired by selecting suitably component composition of two or more microbially degradable resin mixture, and component composition of two or more polyolefine system resin mixture. Thus, the film obtained usually has preferably 3-1000 micrometers of the thickness of about 5-500 micrometers.

[0011] The rate of a polyolefine system resin of the rate of the microbially degradable resin in the above-mentioned resin film is 40 - 15 % of the weight preferably 50 to 10% of the weight 60 to 85% of the weight 50 to 90% of the weight. Generally, when a microbially degradable resin is disassembled by the microorganism, in order that a decay of a resin film may happen, with many the loadings tends to collapse. However, if the rate exceeds the aforementioned domain, the machine physical properties of a film will get worse and it will stop being equal to practical use as film weld field. If the content of a microbially degradable resin comes to exceed 90 % of the weight especially, the **** elasticity of the film obtained becomes high too much, it will be divided and the value **** in suppleness which it is as a film will fall to a film remarkably. On the other hand, when there are few rates of the microbially degradable resin than the aforementioned domain, the heat-sealing intensity of the film obtained falls.

[0012] The above-mentioned resin film can contain other supplementary components. For example, the inorganic bulking agent for raising a mechanical strength and the compatibility-ized agent for raising the compatibility of a microbially degradable resin and a polyolefine system resin can be used. As a compatibility-ized agent, there is a copolymer of a microbially degradable resin and a polyolefine system resin. As for such a macromolecule compatibility-ized agent, it is desirable that it is dealt with by a polyolefine system resin and the EQC, and viscosity [in the extrusion temperature] $\eta(C)$ fulfills the conditions of $10 > \eta(C) / \eta(A) \geq 1$. Moreover, ** ON of the blending ratio of coal is carried out to the rate of a polyolefine system resin.

[0013] The above-mentioned resin film may be a foaming film. When obtaining a foaming film, it is desirable to make a melting kneading object contain a foaming agent, and to carry out extrusion from the die at the nose of cam of an extruder to a low-pressure-zone region. In this case, the quality foaming film which does not have irregularity in a front face highly [it is desirable to perform melting kneading in front of foaming agent injection on the conditions with which it is satisfied of a following formula (3) and a following formula (4), and / the rate of a closed cell] by this can be obtained easily.

$$0.6 \leq \eta(B) / \eta(A) \leq 5 \quad (3)$$

$$\eta(A) \leq 500 \quad (4)$$

$\eta(A)$ shows the melt viscosity (poise) of the microbially degradable resin in the degree of melting kneading temperature in front of foaming agent injection among a formula, and $\eta(B)$ shows the melt viscosity (poise) of the polyolefine system resin in the melting kneading temperature in front of foaming agent injection. In addition, it is so desirable that the mixed rate of the value of the above-mentioned formula (1), and $\eta(B) / \eta(A)$ in (3) (A) of a microbially degradable resin generally increases to make it small in the above-mentioned domain. Therefore, it is necessary to calculate the desirable value in each blending ratio of coal by the preliminary experiment.

[0014] It is desirable independent or to mix and to use the chlorofluocarbon which has one or more

hydrogen atoms into aliphatic hydrocarbon, a halogenated hydrocarbon, or a molecule, as the aforementioned foaming agent, in mainly aiming at inside or a high foaming. As an example of aliphatic hydrocarbon, a propane, normal butane, an isobutane, a pentane, an isopentane, etc. are mentioned, and the chlorine or the bromination field of these aliphatic hydrocarbon is mentioned as a halogenated hydrocarbon. Moreover, as chlorofluocarbon which has one or more hydrogen atoms in a molecule, they are clo ***** methane, ***** methane, 1, 2 and 2, 2-tetrapod ***** ethane, 1-***** -1, 1-***** ethane, 1 and 1, - ***** ethane, and 1-***** - 1, 2, 2, and 2-tetrapod ***** ethane etc. is mentioned. It faces using the above-mentioned **** foaming agent, and the boiling point (under 1 normal atmosphere) needs to choose a thing 80 degrees C or less. In that by which the above-mentioned boiling point exceeds 80 degrees C, foaming luminous efficacy is inferior and uneconomical. It is desirable to choose that whose above-mentioned boiling range is -20-20 degrees C as a principal component especially as a foaming agent. Moreover, when especially aiming at a low foaming, use of the combination of the acid-alkali which reacts at the chemistry foaming agent which decomposes at the temperature in an extruder and generates gas, for example, a sodium bicarbonate, an ammonium carbonate, an azide compound, azobis isobutyl nitril, a diazoaminobenzene, benzene sulfonylhydrazide, P-tosyl hydrazide, or this temperature, and generates carbon dioxide gas, for example, the alkali-metal salt of the mono-alkali-metal salt-carbonic acid of a citric acid, the alkali-metal salt of the mono-alkali-metal salt-pile carbonic acid of

[0015] When obtaining a foaming film, the operating rate of a foaming agent is suitably defined according to 0.1 - 60 weight section and the density of the foaming film for which is 0.2 - 50 weight section preferably, and it asks to the total quantity 100 weight section of a microbially degradable resin and a polyolefine system resin. The technique of extruding an additive in the shape of a film under low voltage as a foaming method through the die which carries out melting kneading within an extruder and is located subsequently to an extruder nose of cam a foaming agent, a resin, and if needed is employable. Thus, as for the thickness of the film obtained, it is desirable to be referred to as about 10-300 micrometers. In this invention, in order to obtain the good foaming film of a microorganism collapsibility, it is required for the foaming film to make sufficient foaming structure hold. The good foaming film of a microorganism collapsibility can be obtained by specifying the mean foam thickness which generally constitutes 0.5-0.01g /of 3 and foaming films for the apparent density of a foaming film cm preferably three or less [0.75g //cm] to 1-100 micrometers. The rate of a closed cell in a foaming film is 90 - 100% of a domain preferably 80% or more.

[0016] As described above, the amount of the foaming agent used and the amount of the so-called cellular nucleating additive used can adjust the density and the cellular thickness of a foaming film easily. As this cellular nucleation agent, for example Talc, a calcium carbonate, a magnesium carbonate, Clay, a natural silicic acid, carbon black, white carbon, milt, The mineral matter like plaster, or the chemistry foaming agent which decomposes at the temperature in an extruder and generates gas, For example, a sodium bicarbonate, an ammonium carbonate, an azide compound, azobis isobutyl nitril, The acid-alkali which reacts at a diazoaminobenzene, benzene sulfonylhydrazide, P-tosyl hydrazide, or this temperature, and generates carbon dioxide gas combines. for example The alkali-metal salt of the mono-alkali-metal salt-carbonic acid of a citric acid, the alkali-metal salt of the mono-alkali-metal salt-pile carbonic acid of a citric acid, etc. are mentioned. When using the above-mentioned mineral matter as a cellular nucleating additive, it is under 5 weight section more than 0.01 weight section to the resin 100 weight section. Moreover, when using the above-mentioned chemistry foaming agent as a cellular nucleating additive, it is 0.05 - 5 weight section similarly.

[0017] Furthermore, in this invention, in order to prevent rapid escaping from the resin of the foaming agent with to a resin if needed and to suppress deflation of a foaming film, a shrinkproofing agent can also be added. As such a thing, for example A polyoxyethylene monochrome millimeter state, A polyoxypropylene monochrome millimeter state, polyoxyethylene monopalmitate, Polyoxypropylene monopalmitate, polyoxyethylene monostearate, Polyoxypropylene monostearate, polyoxyethylene distearate, Mono-lauric-acid glyceride, mono-***** acid glyceride, mono-palmitic-acid glyceride, Monostearin acid glyceride, mono-arachin acid glyceride, ***** acid glyceride, Various aliphatic

ester, such as dipalmitate glyceride, distearic acid glyceride, 1-*****-2-stearin acid glyceride, 1-*****-2-myristic-acid glyceride, and tristearin acid glyceride, is mentioned.

[0018] The film weld field by this invention piles up the plurality of the above mentioned resin film, and is acquired by heat sealing a necessary fraction. A glove, a cellular enclosure pad besides a bag-like object, etc. are included by such thing.

[0019]

[Effect of the Invention] The resin film weld field by this invention has a good microorganism collapsibility. Such a microorganism collapsibility is discovered by mixing of a microbially degradable resin, and the specific internal structure of a film. Since after abandonment can collapse easily in the environment where a microorganism exists and the resin film weld field of this invention can decrease the **, it gives a means effective in a resolution of a waste-treatment problem. Moreover, even if it is left in a natural environment by the recovery leak after abandonment, this film weld field does not expose the life of the animals and plants of a nature to risk, in order to collapse by the microorganism. Since the film weld field of this invention has a high heat-sealing intensity, it does not exfoliate easily from a heat-sealing fraction. As [fracture / easily / and / when it pulls / since it excels in **** physical properties / it] As [produce / a white blush mark / when it pulls, without surface / a part of / exfoliating even if it rubbed the front face / furthermore,] And it has a ductility as a film. Thus, the film weld field of this invention improves remarkably in the practicality.

[0020]

[Example] Next, an example explains this invention still in detail.

The example 1 poly caprolactone (PCL), and a low density polyethylene (LDPE) or a denaturation polyolefine was blended at a rate of Table 1, melting kneading of this compound was carried out within the extruder, and this melting kneading object was fabricated with the inflation equipment with a die with a diameter of 100mm on the film with a thickness of about 50 micrometers (about 160 degrees C of extrusion temperatures). However, it was accepted example of comparison 3 and the cast film with a thickness of about 50 micrometers was obtained by the T die method (300mm of die widths) (about 230 degrees C of extrusion temperatures).

[0021] Next, measurement of a heat-sealing intensity, **** physical properties, and a microorganism collapsibility was performed as follows about the obtained film. Moreover, the wear nature of a film was measured as follows. The result is shown in Table 2.

(1) It is JIS about a heat-sealing on-the-strength sample. It considered as the shape (the width of face of 10mm of a parallel part, the length of 40mm) of K6767 dumbbell, it carried out in the length orientation at 2 chip boxes, and the impulse sealer (heating 1.5 seconds, and cooling 3 seconds) performed the parallel part (5x10mm of seals). Measurement of a heat-sealing intensity was performed using the tensile strength testing machine by 50mm of the distance between chucks, 50mm of speed of testings, and min.

(2) **** physical properties (breaking strength, fracture elongation, elastic modulus)

It is JIS about a sample. It considered as the shape (the width of face of 10mm of a parallel part, the length of 40mm) of K6767 dumbbell, and carried out using the tensile strength testing machine by 90mm of the distance between chucks, 500mm of speed of testings, and min. In fracture elongation, the elongation between the chucks to fracture was measured and it computed at a rate over 40mm of the parallel parts of a sample (%). Moreover, the calculation technique of breaking strength and an elastic modulus is JIS. K7113 was followed. In addition, the elongation between the chucks to 40mm of the parallel parts of a sample showed the strain (elongation) adopted with the elastic modulus.

(3) The wear nature sample was set to 50x50mm, and it carried out to the same film using the abrasion tester on stroke 20mm, both-way speed 60 batch, and the conditions of 3000g of loads. The following criteria estimated the test result.

On he has no appearance change over :10 minutes -- [0022] which could delete the film front face less than [x:1 minute], and nebula produced (4) 0.3ml of the lipase solutions which have the potency which can generate the fatty acid of 130micromole in 1 minute from microorganism collapsibility examination olive oil, They are 2ml and a surfactant (tradename "ply surfboard A210G" which is the Dai-Ichi Kogyo

Seiyaku Co., Ltd. make 1ml) about a phosphate buffer solution (pH7). 16.7ml of water and 100mg of each sample were paid to 100ml Erlenmeyer flask, it was made to react finally at 30 degrees C for 16 hours, and the organic amount of resources generated after the reaction was measured by the total-organic-carbon concentration meter. In case of measurement, what does not use a lipase solution by the same technique as a control experiment was carried out, and measured value was rectified.

[0023] In addition, in a denaturation polyolefine, EEA shows ethylene / ethyl-acrylate copolymerization resin (ethyl-acrylate content 10wt%), and EVA shows ethylene / vinyl acetate copolymerization resin (vinyl acetate content 15wt%). LDPE shows a low density polyethylene. moreover, a carbonyl inclusion monomer [as opposed to the whole resin in the carbonyl inclusion monomer content shown in Table 1] (ethyl acrylate or vinyl acetate) -- comparatively (wt%) -- being shown .

[0024]

[Table 1]

番号		配合比 (重量%)			カルボニル含有 モノマー含有率 (wt %)
		PCL	LDPE	変性ポリオレフィン	
実 施 例	1	60	—	EEA : 40	4.0
	2	70	—	EEA : 30	3.0
	3	70	—	EVA : 30	4.5
	4	80	—	EVA : 20	3.0
比 較 例	1	70	30	—	—
	2	40	—	EEA : 60	6.0
	3	95	—	EVA : 5	1.5

[0025]

[Table 2]

Table 2

番 号		ヒートシール強度 (gf/cm)	引張物性			微生物崩壊性	摩耗性
			破断強度 (kgf/mm ²)	破断伸び (%)	弾性率 (kgf/cm ²)	有機物質 (ppm)	
実 施 例	1	560	1.91	840	1180	209	○
	2	740(材料破壊)	1.91	800	1230	448	○
	3	610(材料破壊)	2.23	980	1200	432	○
	4	720(材料破壊)	2.35	960	1260	490	○
比 較 例	1	600	1.18	560	1670	502	×
	2	190	1.73	840	1160	160	○
	3	750	1.83	590	2580	542	○

[0026] The film weld field of this invention has the outstanding **** physical properties and the outstanding microorganism collapsibility while it shows a high heat-sealing intensity so that the result

shown in Table 2 may show. Moreover, it excels in abrasion resistance and front ***** of a film is not produced in an abrasion test. On the other hand, the film weld field (example 1 of a comparison) which does not contain a denaturation polyolefine is inferior to **** physical properties and abrasion resistance a still inadequate top in a heat-sealing intensity. Moreover, in the case (example 2 of a comparison) where there are too few aliphatic polyester components, a heat-sealing intensity falls extremely. On the other hand, in the case (example 3 of a comparison) where there are too many aliphatic polyester components, the modulus of elasticity in tension of a film became large too much, and became what lacks in a ductility.

[Translation done.]